(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 271 195**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **87309489.0**

(22) Date of filing: **27.10.87**

(51) Int. Cl.4: **C07D 251/24** , G03C 1/68 , G03F 7/10

Claims for the following Contracting State: ES.

(30) Priority: **12.11.86 GB 8627059**

(43) Date of publication of application:
15.06.88 Bulletin 88/24

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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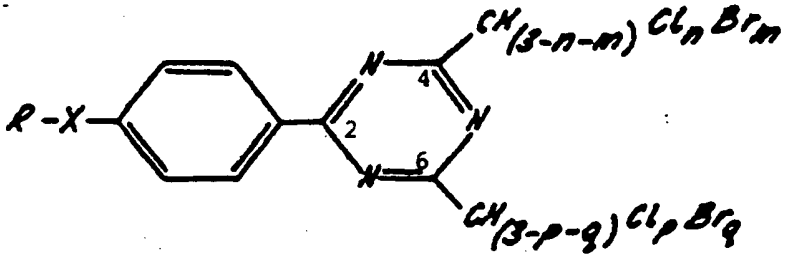
(54) **Substituted triazine derivatives.**

(57) A triazine derivative of the formula



wherein R is an alkyl group or an aryl group,
X is S, Se or Te,
n or m is 0, or each is an integer of from 1 to 3, the total sum of n + m not being greater than 3, and p or q is 0, or each is an integer of from 1 to 3, the total sum of p + q not being greater than 3. The triazines may be used in photopolymerizable compositions.

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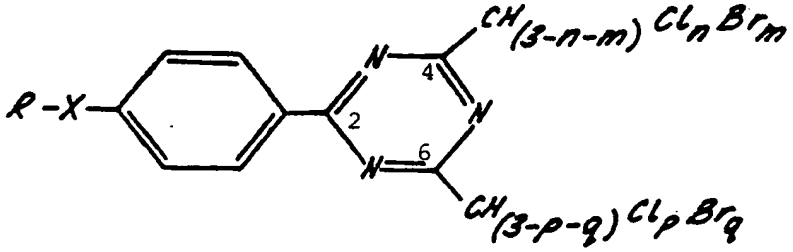
SUBSTITUTED TRIAZINE DERIVATIVES

The present invention relates to substituted triazine derivatives and, in particular, to substituted triazine derivatives which contain a chalcogenide substituent.

2-Substituted-4,6-bis(trihalomethyl)-1,3,5-triazines have been used to initiate photopolymerisation in photosensitive resin compositions (e.g. JP60/60104, 6th April, 1985, Fuji Photo Film Co. Ltd) and to generate strong colour changes on exposure of positive-acting compositions (e.g. US 4350753, 21st September, 1982, Polychrome Corp.)

We have now developed certain substituted triazine derivatives which can initiate polymerization or generate strong colour changes. These compounds contain a 4-alkylthiophenyl, 4-arylthiophenyl group, or the selenium or tellurium analogues thereof, and absorb more strongly at the wavelengths commonly used in lithographic print down frames (exposure units) than do structurally similar triazines which do not contain the sulphur, selenium or tellurium linkages.

Accordingly, the present invention provides a triazine derivative of the general formula:



wherein R is an alkyl group or an aryl group,

X is S, Se or Te,

n or m is 0, or each is an integer of from 1 to 3, the total sum of n + m not being greater than

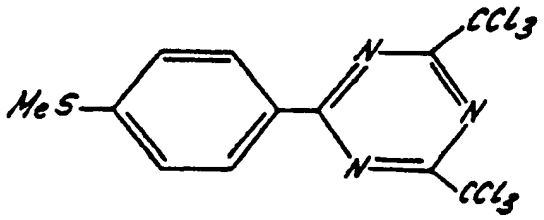
3, and

p or q is 0, or each is an integer of from 1 to 3, the total sum of p + q not being greater than 3.

Preferably, the compounds of the invention are compounds in which the substituents at positions 4 and 6 of the triazine group are identical. More preferably n is 3, m is 0, p is 3 and q is 0.

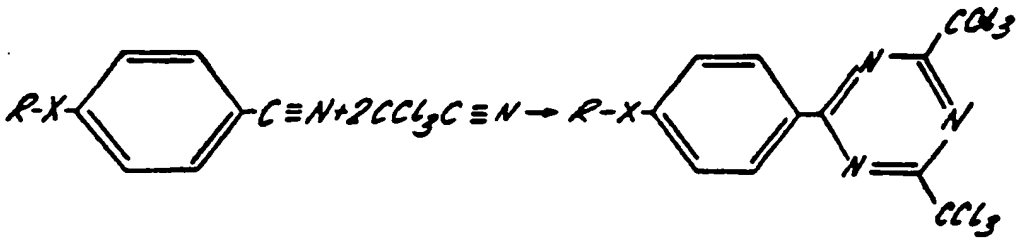
The group R is preferably an alkyl group containing from 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms, most preferably a methyl or ethyl group, or a phenyl or substituted phenyl group.

A preferred compound of the present invention is 2-(4-methylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, which has the following formula:



Other preferred compounds of the invention are 2-(4-ethylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-stearylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-phenylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-(4-methoxyphenyl)thiophenyl)-4,6-bis-trichloromethyl)-1,3,5-triazine and 2-(4-methylthiophenyl)-4,6-bis(tribromomethyl)-1,3,5-triazine.

The compounds of the present invention may be prepared by the general method described in Bull. Chem. Soc. Japan, 1969, 42, pages 2924 to 2930, by cotrimerization of the halogenated acetonitrile with a substituted benzonitrile, in the presence of hydrochloric acid and a Friedel-Crafts catalyst, e.g. $AlCl_3$, $AlBr_3$, $TiCl_4$, or boron trifluoride etherate. A typical reaction sequence is given below:



Other ways of synthesizing the compounds are by reacting aryl amidines with polychloroaza-alkenes according to the method published in Angew., Chem., 1966, 72, p. 982 et seq. Methods for the subsequent chlorination and bromination of alkyl substituents in s-triazines and exchange reaction in which bromine atoms in tribromomethyl groups may be replaced by hydrogen are disclosed in J. Org. Chem., 1964, 29, p. 1527 et. seq. Some of the nitriles used in the co-trimerization may be prepared by simple methods known in the art, for example by the dehydration of carboxylic acid amides or oximes, or by the reaction of aromatic bromine compounds with cuprous cyanide.

The compounds of the present invention are photo-initiators, i.e. initiate polymerization reactions, and/or are capable of causing colour changes in coloured systems.

For use as photoinitiators, the compounds of the present invention are effective in amounts of from about 0.05 to 20 percent by weight, with amounts in the range of up to 10 percent by weight and more preferably from 3 to 7 percent by weight being particularly preferred. The photoinitiators may be used, for example, to initiate photopolymerization reactions which are triggered by free radicals. Suitable monomers which can be photopolymerized are acrylates, methacrylates, vinyl esters and vinylamides. The polymerizable compositions may contain conventional additives, such as fillers,

dyestuffs, plasticizers or polymerization inhibitors.

The compounds of the present invention are also capable of causing colour changes in coloured systems during photolysis or of initiating colour formation in colour couplers, e.g. leuco compounds. Colour changes are of particular importance in the manufacture of lithographic plates because they make it possible for the plates to be examined before they are developed. It is well known that depending upon the composition of the radiation-sensitive coating employed a lithographic printing plate may reproduce the image to which it is exposed, in which case it is termed a positive-working plate, or it may produce an image complementary to the one to which it is exposed, in which case it is termed a negative-working plate. The compounds of the present invention may be used in either positive-working or negative-working lithographic plates.

Accordingly, the present invention also includes within its scope a coating composition for a positive-working or a negative-working lithographic printing plate which comprises from 0.05 to 20 percent by weight of total solids of a novel substituted triazine of the invention. Preferably these compositions comprise up to 10 percent, more preferably from 1 to 7 percent by weight, and most preferably about 5 percent by weight of total solids of the novel substituted triazine.

The present invention will be further described with reference to the following Examples.

EXAMPLE 1

Synthesis of 2-(4-methylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine.

4-(Methylthio)benzonitrile (24.5 g), trichlorocetonitrile (47.8 g) and aluminium tribromide (0.48 g), were placed in a 3-necked flask, and the mixture was saturated with gaseous HCl whilst being maintained at a temperature of from -10 to 0°C for 3 hours. After standing for 2 days the mixture was heated and poured into water (2 litres); the precipitated solids were filtered and recrystallised from ethanol - yield 70%.

m.p. 149-151°C.

I.R. (KBr) 695, 720, 770, 820, 845, 1020, 1090, 1190, 1340, 1400, 1510, 1550, 1595, 2925 cm^{-1}

U.V. (EtOH) λ_{max} 358nm, ε_{max} 37,960 1 mol^{-1} cm^{-1}
λ_{max} 235nm, ε_{max} 12,300 1 mol^{-1} cm^{-1}

N.M.R. ($CDCl_3$) δ 2.6(3H,s),7.3(2H,d),8.5(2H,d).

Example 2

Synthesis of 2-(4-ethylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine

4-(Ethylthio)benzonitrile (3.0g), trichloroacetonitrile (8g) and aluminium tribromide (0.1g) were placed in a 3-necked flask and the mixture was saturated with gaseous HCl whilst being maintained at a temperature of from -5 to +5°C for 30 minutes. After standing for 3 days, the mixture was heated and poured into methanol (500ml); the precipitated solids were filtered and recrystallised from ethanol - yield 68%.

m.p. 112-113°C

I.R. (Nujol) 695, 770, 820, 845, 920, 990, 1010, 1090, 1110, 1140, 1190, 1345, 1395, 1505, 1550, 1595 cm^{-1}

U.V. (EtOH) λ_{max} 362nm, ε_{max} 11,300 1 mol^{-1} cm^{-1}
λ_{max} 237nm, ε_{max} 3,950 1 mol^{-1} cm^{-1}

N.M.R. ($CDCl_3$) δ 1.4(3H,t), 3.1(2H,q), 7.4(2H,d), 8.6(2H,d).

Example 3

Synthesis of 2-(4-stearylthiophenyl)-4,6-bis-(trichloromethyl)-1,3,5-triazine

4-(Stearylthio)benzonitrile (10g), trichloroacetonitrile (10g) and aluminium tribromide (0.3g) were placed in a 3-necked flask and the mixture saturated with gaseous HCl whilst being maintained at a temperature of 50°C for 30 minutes. After standing for 3 days the mixture was heated and poured into methanol (1 litre); the precipitated solids were collected and recrystallised from ethanol - yield 49%.

m.p. 64-66°C

I.R. (Nujol) 670, 695, 715, 720, 770, 780, 820, 850, 920, 990, 1010, 1090, 1185, 1340, 1400, 1510, 1545, 1595 cm^{-1}

U.V. (EtOH) λ_{max} 365nm, ε_{max} 18,400 1 mol^{-1} cm^{-1}
λ_{max} 235nm, ε_{max} 2,900 1 mol^{-1} cm^{-1}

N.M.R.($CDCl_3$) δ 0.9(3H,m), 1.25(32H,m), 3.1(3H,t), 7.4(2H,m), 8.6(2H,m).

Example 4

Synthesis of 2-(4-phenylthiophenyl)-4,6-bis-(trichloromethyl)-1,3,5-triazine

4-(Phenylthio)benzonitrile (1.6g), trichloroacetonitrile (2.2g) and aluminium tribromide (0.1g) were placed in a 3-necked flask, and the mixture was saturated with gaseous HCl whilst being maintained at a temperature of from -10 to 0°C for 30 minutes. After standing for 3 days the mixture was heated and poured into methanol (500ml); the precipitated solids were collected and recrystallised from ethanol - yield 63%.

m.p. 111-112°C

I.R. (Nujol) 665, 700, 725, 770, 780, 810, 830, 855, 925, 1015, 1080, 1115, 1190, 1250, 1350, 1400, 1500, 1555, 1595 cm^{-1}

U.V.(EtOH) λ_{max} 358nm, ε_{max} 24,400 1 mol^{-1} cm^{-1}

N.M.R.($CDCl_3$) δ 7.2(2H,m), 7.4-7.6(5H,m), 8.5(2H,m).

Example 5

Synthesis of 2-(4-(4-methoxyphenyl)thiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine

4-(4-Methoxyphenylthio)benzonitrile (3g), trichloroacetonitrile (3.6g) and aluminium tribromide (0.1g) were placed in a 3-necked flask, and the mixture was saturated with gaseous HCl whilst being maintained at a temperature of -10° to 0°C for 30 minutes. After standing for 3 days the mixture was heated and poured into methanol (500ml); the precipitated solids were collected and recrystallised from ethanol - yield 64%.

m.p. 136-137°C

I.R. (Nujol) 665, 700, 720, 775, 815, 830, 835, 855, 925, 960, 970, 990, 1015, 1025, 1080, 1100, 1110, 1115, 1175, 1185, 1250, 1290, 1300, 1350, 1360, 1400, 1500, 1555, 1595 cm^{-1}.

U.V. (EtOH) λ_{max} 228nm, ε_{max} 25,000 $l \cdot mol^{-1} cm^{-1}$
λ_{max} 284nm, ε_{max} 36,300 $l\ mol^{-1} cm^{-1}$
λ_{max} 361nm, ε_{max} 3,600 $l\ mol^{-1} cm^{-1}$

N.M.R.($CDCl_3$) δ 3.8(3H,m),6.9(2H,m),7.1(2H,m) 7.5(2H,m),8.5(2H,m).

Example 6

Synthesis of 2-(4-methylthiophenyl)-4,6-bis(tribromomethyl)-1,3,5-triazine

4-(Methylthio)benzonitrile (5g), tribromoacetonitrile (23g) and aluminium tribromide (0.7g) were placed in a 3-necked flask, and the mixture was saturated with gaseous HCl whilst being maintained at a temperature of 15° to 25°C for 30 minutes. After standing for 3 days, the mixture was heated and poured into methanol (1 litre), the mixture heated and the precipitated solids collected - yield 36%.

m.p. 156-157°C

I.R. (Nujol) 620, 660, 695, 740, 815, 1090, 1536, 1590 cm^{-1}

U.V. (EtOH) λ_{max} 235nm, ε_{max} 22,900 l mol^{-1} cm^{-1}
λ_{max} 355nm, ε_{max} 41,100 l mol^{-1} cm^{-1}

N.M.R. ($CDCl_3$) δ 8.6(2H,d),7.4(2H,d) 2.6(3H,s).

EXAMPLE 7

A coating composition was prepared from the following ingredients:

10 ml 20% naphthoquinone diazide/novolak resin in oxitol

2 ml 1% Basonyl Blue in dimethylformamide

2 ml 1% Ethyl Violet in dimethylformamide

5 ml 1% 2-(4-methylthiophenyl)-4,6-bis(trichlomethyl)-1,3,5-triazine in dimethylformamide

The composition was coated onto anodised aluminium, dried, exposed for 30 seconds in a 5 kW Montakop exposure unit, and developed with an aqueous alkaline developer.

EXAMPLE 8

A coating composition was prepared from the following ingredients:

16 ml 5% cellulose acetate butyrate in dimethylformamide

8 ml 10% polyester acrylate in dimethylformamide

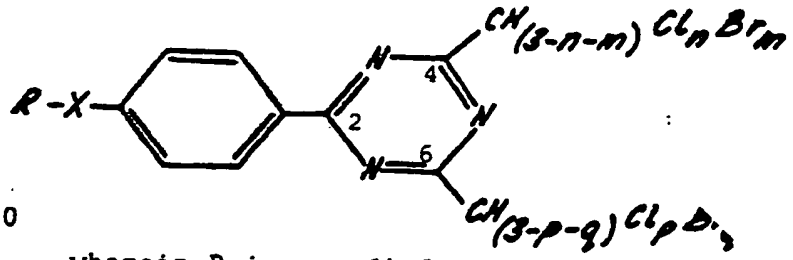
4 ml 10% dipentaerythritol monohydroxypentaacrylate in dimethylformamide

10 ml 1% 2-(4-methylthiophenyl)-4,6-bis(trichlomethyl)-1,3,5-triazine in dimethylformamide.

The composition was coated onto anodised aluminium, dried, optionally overcoated with poly(vinyl alcohol), exposed, and developed with an organic solvent developer.

CLAIMS:

1. A novel triazine derivative of the formula



wherein R is an alkyl group or an aryl g.

X is S, Se or Te,

n or m is 0, or each is an integer of from 1 to 3, the total sum of n + m not being greater than 3, and p or q is 0, or each is an integer of from 1 to 3, the total sum of p + q not being greater than 3.

2. A compound as claimed in claim 1 wherein the triazine group contains identical substituents at positions 4 and 6 thereof.

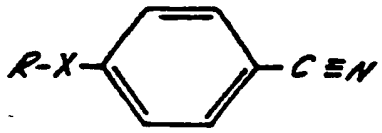
3. A compound as claimed in claim 1 or claim 2 wherein n is 3, m is 0, p is 3 and q is 0.

4. A compound as claimed in any one of the preceding claims wherein R is an alkyl group containing from 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms.

5. 2-(4-Methylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-ethylthiophenyl)-4,6-bis-(trichloromethyl)-1,3,5-triazine, 2-(4-stearylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-phenylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-(4-methoxyphenyl)-thiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine

or 2-(4-methylthiophenyl)-4,6-bis(tribromomethyl)-1,3,5-triazine.

6. A process for the preparation of a symmetrically substituted triazine compound as claimed in claim 2 which comprises reacting a substituted benzonitrile of the formula:



wherein R and X are as defined above, with a halogenated acetonitrile of the formula

$$CH_{(3-n-m)}Cl_nBr_mC{\equiv}N$$

wherein n or m is 0, or each is an integer of from 1 to 3, the total sum of n + m not being greater than 3, in the presence of hydrochloric acid and a Friedel-Crafts catalyst.

7. A photopolymerizable composition which comprises at least one photopolymerizable monomer and from 0.05 to 20 percent by weight of at least one compound as claimed in any one of the preceding claims.

8. A coating composition for a positive-working or negative-working lithographic plate which comprises from 0.05 to 20 percent by weight of total solids of at least one compound as claimed in any one of claims 1 to 5.

9. A composition as claimed in claim 8 which comprises from 1 to 7 percent by weight of total solids of at least one compound as claimed in any one

of claims 1 to 5.

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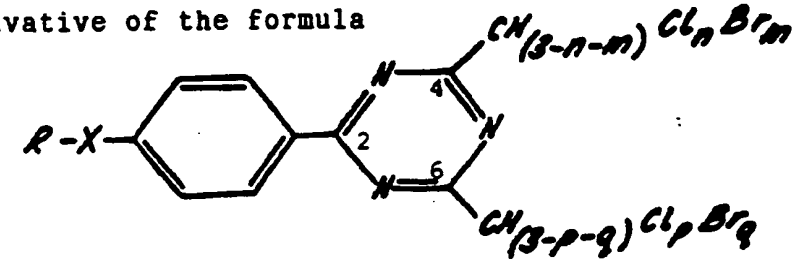
CLAIMS:

1. A photopolymerizable compostion which comprises at least one photopolymerizable monomer and from 0.05 to 20 percent by weight of at least triazine derivative of the formula



wherein R is an alkyl group or an aryl group,

X is S, Se or Te,

n or m is 0, or each is an integer of from 1 to 3, the total sum of n + m not being greater than 3, and p or q is 0, or each is an integer of from 1 to 3, the total sum of p + q not being greater than 3.

2. A composition as claimed in claim 1 wherein the triazine group of the triazine derivative contains identical substituents at positions 4 and 6 thereof.

3. A composition as claimed in claim 1 or claim 2 wherein the triazine derivative is one in which n is 3, m is 0, p is 3 and q is 0.

4. A composition as claimed in any one of the preceding claims wherein the triazine derivative is one in which R is an alkyl group containing from 1 to 20 carbon atoms, preferably 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms.

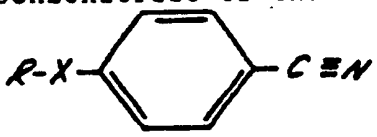
5. A composition as claimed in any one of the preceding claims wherein the triazine derivative is 2-(4-methylthiophenyl)-4,6-bis(trichloro-methyl)-1,3,5-

triazine, 2-(4-ethylthiophenyl)-4,6-bis-(trichloromethyl)-1,3,5-triazine, 2-(4-stearylthiophenyl)-4,6-bis-(trichloromethyl)-1,3,5-triazine, 2-(4-phenylthiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine, 2-(4-(4-methoxyphenyl)-thiophenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine or 2-(4-methylthiophenyl)-4,6-bis(tribromomethyl)-1,3,5-triazine.

6. A coating composition for a positive-working or negative-working lithographic plate which comprises from 0.05 to 20 percent by weight of total solids of at least one triazine derivative as defined in any one of claims 1 to 5.

7. A composition as claimed in claim 6 which comprises from 1 to 7 percent by weight of total solids of at least one triazine derivative as claimed in any one of claims 1 to 5.

8. A process for the preparation of a symmetrically substituted triazine compound as defined in claim 2 which comprises reacting a substituted benzonitrile of the formula:



wherein R and X are as defined above, with a halogenated acetonitrile of the formula

$$CH_{(3-n-m)}Cl_nBr_mC{\equiv}N$$

wherein n or m is 0, or each is an integer of from 1 to 3, the total sum of n + m not being greater than 3, in the presence of hydrochloric acid and a Friedel-Crafts catalyst.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 30 9489

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	GB-A-2 029 428 (FUJI) * Page 6, lines 5-9; pages 7-11; claims 1,23 * ---	1,7,8	C 07 D 251/24 G 03 C 1/68 G 03 F 7/10
Y	FR-A-1 481 819 (DU PONT) * Page 1, column 1 - page 4, column 1; page 9, column 2, lines 15-40; page 11, column 2, line 21 - page 12, line 13; claims 1-7 * -----	1,7,8	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 07 D 251/00
G 03 C 1/00
G 03 F 7/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17-02-1988	BRENNAN J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

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